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Competitive Reactions Determining Fate of ^{95g}Tc in Pertechnetate Solutions

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Isomeric transition / ^{95m}Tc / *Exchange reactions* / TcO_4^-

Summary

The retention of ^{95g}Tc as TcO_4^- in solutions of ^{95m}Tc/$^{99}TcO_4^-$ is dependent on the pertechnetate concentration at values above 6×10^{-3} *M*. It is also affected by the presence of different concentrations of Tc(IV) carriers. At the higher pertechnetate concentrations the retention is influenced by the nature of the alkali metal co-cation. The results suggest that a product of the isomeric transition can form $^{95g}TcO_4^-$ by an electron transfer reaction with $^{99}TcO_4^-$.

1. Introduction

In an earlier report [1] a rather surprising difference between the proportion of ^{95g}Tc forming TcO_4^- was found when isomeric transition took place in solutions of lithium and potassium pertechnetates. This result warranted a more detailed study. Preliminary results revealed complications arising from the pertechnetate concentration and the carrier Tc(IV) used. A systematic study of these effects has now been made.

2. Experimental

2.1. Preparation of labelled pertechnetate

Aqueous solutions of $Li^{99}TcO_4$ and $K^{99}TcO_4$ were prepared as described previously [1]. The Tc concentration was determined in each case by measuring the ^{99}Tc with a Packard TRI-CARB 460 CD liquid scintillation system.

The samples of known $^{99}TcO_4^-$ concentration were mixed with carrier-free aqueous solutions containing the corresponding salt (Li or K) of $^{95m}TcO_4^-$ and then evaporated to dryness under reduced pressure. The ^{95m}Tc-labelled pertechnetates were then dissolved in an amount of carrier solution (pH = 2.8) calculated to give the desired $^{99}TcO_4^-$ concentration. The solutions were saturated with nitrogen and stored in the dark at 276 K to reach the transient equilibrium of the ^{95m}Tc/^{95g}Tc isomeric pair.

2.2. Preparation of Tc(IV) carrier solutions

Carrier A: a known amount of $(NH_4)_2{}^{99}TcCl_6$ was dissolved in 100 µl of water and the pH adjusted to 2.8 with acetic acid and lithium hydroxide solution. The technetium concentration of the final solution was 4.5×10^{-3} *M*.

Carrier B: this was prepared in a similar way from $K_2{}^{99}TcCl_6$ and the pH adjusted to 2.8 with sodium acetate and acetic acid. The technetium concentration was 4.5×10^{-3} *M*.

Freshly prepared carrier solutions were used, except where noted for diluted carrier A. The final carrier concentrations used are recorded in the Tables giving results. Spectrophotometric and electrophoretic examination failed to reveal any TcO_4^- in the carriers, even after one week storage under nitrogen.

2.3. Separation procedure

After the establishment of transient equilibrium the different technetium species were separated by low voltage electrophoresis [1]. The supporting electrolyte was 1 *M* H_2SO_4 but in some experiments acetate buffer solution at pH = 3 was also used. No essential differences were found in distribution using the two methods.

3. Results

3.1. Effect of the TcO_4^- concentration

3.1.1. In $LiTcO_4$ *solutions*

The distribution of the ^{95g}Tc as a function of the TcO_4^- concentration, using carrier A to give a technetium concentration of 7.5×10^{-4} *M*, is shown in Fig. 1a. Air-free, nitrogen saturated solutions were used. No appreciable (1%) part of the ^{99}Tc is found other than as TcO_4^-; there is no evidence of any autoradiolysis of the $^{99}TcO_4^-$.

Above about 10^{-3} *M* in TcO_4^- the retention as $^{95g}TcO_4^-$ rises at the expense of the cationic and uncharged products. The precise identity of these products is uncertain. But, except for the anionic product they show similar electrophoretic characteristics to the cationic and neutral species formed in the aquation of $TcCl_6^{2-}$.

The distribution of the ^{95g}Tc proved to be sensitive to the carrier used. Table 1 records the ^{95g}Tc distribution found using carrier B, giving a technetium concentration of 4.5×10^{-3} *M*. The retention as $^{95g}TcO_4^-$ is still dependent on the TcO_4^- concentration, but it is smaller than in the experiments using carrier A. The decrease in the proportion of $^{95g}TcO_4^-$ is reflected in an increase in

Table 1. *Chemical distribution of* ^{95g}Tc *in* $Li^{99(95m)}TcO_4$
Carrier B: giving Tc concentration due to carrier alone of 4.5×10^{-3} *M*.

Conc. of $LiTcO_4$ (*M*)	Ethanol (%)	Ambient atmosphere	$^{95g}TcO_4^-$ (%)	Uncharged species (%)	Cationic species (%)	Anionic species (%)
Carrier-free $Li^{95m}TcO_4$ sol.	–	N_2	17.9 ± 1.5	40.4 ± 3.5	26.2 ± 2.7	15.5 ± 1.9
	–	air	15.3 ± 3.7	44.8 ± 3.4	20.8 ± 2.5	19.1 ± 3.5
6×10^{-5}	–	N_2	17.7 ± 2.5	43.7 ± 2.5	17.5 ± 0.9	21.1 ± 2.9
6×10^{-3}	–	air	21.5 ± 3.2	41.7 ± 1.2	23.8 ± 2.5	13.0 ± 3.5
6×10^{-3}	–	N_2	21.7 ± 2.3	44.0 ± 2.1	22.6 ± 2.7	11.7 ± 2.8
6×10^{-3}	10%	N_2	21.6 ± 3.2	44.6 ± 1.7	18.8 ± 2.4	15.0 ± 3.2
6×10^{-3}	25%	N_2	30.1 ± 3.3	35.4 ± 3.5	18.2 ± 2.9	16.3 ± 2.4
10^{-2}	–	N_2	27.5 ± 1.9	25.6 ± 1.5	25.6 ± 1.2	21.3 ± 2.5

the uncharged product. This becomes the dominant form of ^{95g}Tc whenever carrier B is used.

Another difference between the two carriers is found in the influence of dissolved air or oxygen. As seen in Table 2 the proportion of $^{95g}TcO_4^-$ increases in the presence of dissolved oxygen when carrier A is used but does not when carrier B is used.

Table 2. *Influence of* O_2 *on the* $^{95g}TcO_4^-$ *yield in* $Li^{99(95m)}TcO_4$ *solution*

Carrier (*M*)	$^{99}TcO_4^-$ (*M*)	$^{95g}TcO_4^-$ (%)	
		N_2	O_2
A, conc = 7.5×10^{-4}	6×10^{-4}	35.5 ± 2.0	42.6 ± 2.5
,,	6×10^{-3}	43.1 ± 2.5	51.5 ± 2.9
B, conc = 3.5×10^{-4}	6×10^{-4}	29.2 ± 3.0	29.9 ± 3.2
,,	6×10^{-3}	42.7 ± 1.8	39.3 ± 3.0

The distribution of the ^{95g}Tc is also dependent on the amount of the carrier used. Data are recorded in Table 3. But the dependence of the proportion of $^{95g}TcO_4^-$ on the concentration of TcO_4^- in the solution is similar at all concentrations of carrier.

Table 3. *Effect of carrier concentration*

Identification and total conc. of carrier (*M*)	Conc. of $^{99}TcO_4^-$ (*M*)	$^{95g}TcO_4^-$ (%)
B, 4.5×10^{-3}	6×10^{-5}	17.7 ± 2.5
B, 4.0×10^{-4}	6×10^{-5}	27.5 ± 1.6
A, 7.5×10^{-4}	6×10^{-5}	35.0 ± 2.0
A, 7.5×10^{-4}	6×10^{-4}	35.5 ± 2.0
A, 3.5×10^{-4}	6×10^{-4}	42.9 ± 2.6
B, 4.5×10^{-3}	6×10^{-3}	21.7 ± 2.3
B, 4.0×10^{-4}	6×10^{-3}	33.7 ± 2.8
A, 7.5×10^{-4}	6×10^{-3}	43.1 ± 2.5
A, 3.5×10^{-4}	6×10^{-3}	52.7 ± 2.5

3.1.2. In $KTcO_4$ *solutions*

The distribution of the ^{95g}Tc as a function of the TcO_4^- concentration is shown in Fig. 1b. These data have been obtained in the presence of carrier A giving a technetium concentration of 4.4×10^{-4} *M*. The carrier A solution used was, however, several days old.

Although the $^{95g}TcO_4^-$ retention is much higher the dependence on the TcO_4^- concentration is essentially similar to that found for the lithium salt. The cationic product is the most important, as was generally found using carrier A. Some results with carrier B at higher concentration are given in Table 4. The $^{95g}TcO_4^-$ retention is lower, as was always found for the same carrier at higher concentration. In addition the uncharged product has again become the dominant form of ^{95g}Tc, although the proportion of cationic product is nearly as great.

Table 4. *Chemical distribution of* ^{95g}Tc *in* $K^{99(95m)}TcO_4$ *solution*
Carrier B: giving Tc concentration due to carrier alone of 4.5×10^{-3} *M*

Conc. of $K^{99}TcO_4$ (*M*)	$^{95g}TcO_4^-$ (%)	Uncharged species (%)	Cationic species (%)	Anionic species (%)
6×10^{-4}	21.7 ± 2.3	35.8 ± 2.9	33.1 ± 2.9	9.4 ± 1.1
6×10^{-3}	24.8 ± 2.2	33.1 ± 4.1	30.0 ± 3.8	12.1 ± 3.3

For both salts and carriers the proportion of ^{95g}Tc in the anionic product is less sensitive to the TcO_4^- concentration. Experiments at fixed concentration of TcO_4^- and varying amounts of carriers A or B gave similar results to those recorded in Table 3 for the lithium salt. In all cases an increase in carrier concentration leads to a decrease in the $^{95g}TcO_4^-$ retention.

3.2. Chemical nature of the two carriers

The purpose of the carrier solution was to try to stabilize ^{95g}Tc formed in lower oxidation states, particularly as Tc(IV) species, and to reduce the likelihood of aerial oxidation of the primary ^{95g}Tc products back to TcO_4^-. For this purpose a mixture of simple Tc(IV) species, such as that obtained by the aquation of $TcCl_6^{2-}$, seemed to be suitable. It is not surprising that such a carrier solution might display poorly reproducible properties. The solutions are not stable systems but are generally undergoing further slow changes. These include further aquation and, perhaps more important, condensation and aggregation

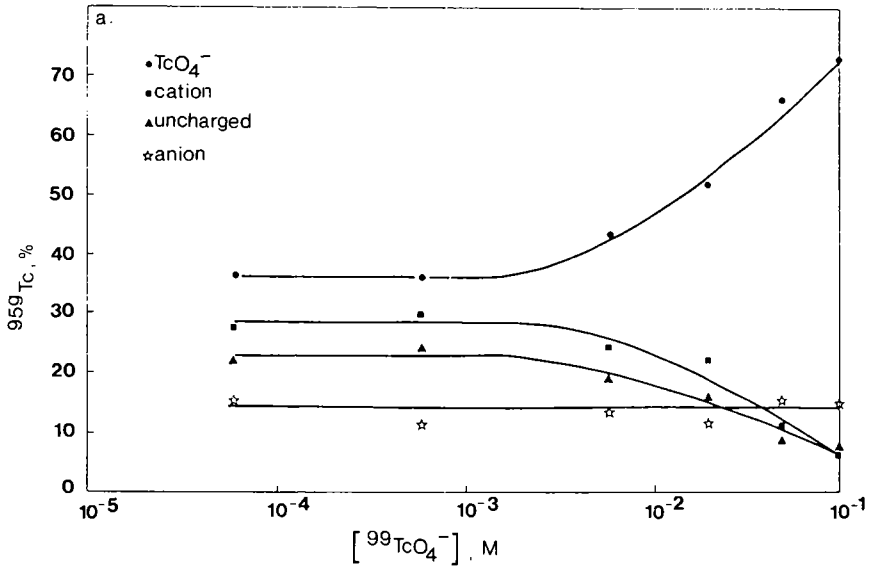

Fig. 1a. Proportion of $^{95g}TcO_4^-$ found in air-free solutions of lithium pertechnetate as a function of the TcO_4^- concentration. Data obtained using solutions containing carrier A to give a technetium concentration of 7.5×10^{-4} *M*.

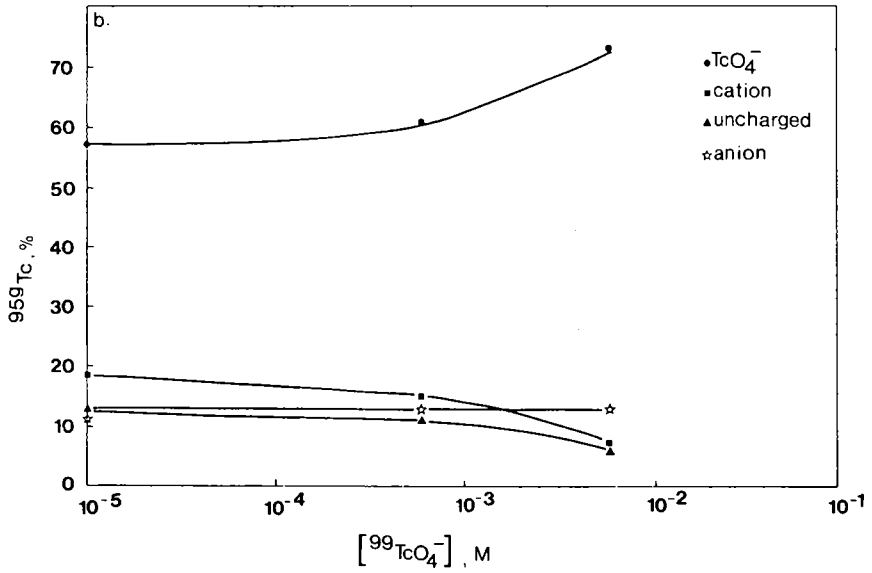

Fig. 1b. Proportion of $^{95g}TcO_4^-$ found in air-free solutions of potassium pertechnetate as a function of the TcO_4^- concentration. Data obtained using solutions containing carrier A to give a technetium concentration of 4.4×10^{-4} *M*.

reactions. These take place with hydroxy species giving products of decreasing solubility that slowly form colloidal aggregates or micelles. Such processes are especially likely with the neutral and cationic aquation products.

A spectrophotometrical examination of the carrier solutions supported the above expectations.

Fig. 2a shows the change of absorption spectrum with time for carrier B. Aquation is incomplete in 4 days, but after 7 days only the cationic product is seen. However, the spectra of the cationic and neutral aquation products, shown in Fig. 2c, reveal rather weak absorptions so that they are not easily estimated in mixtures in this way, nor can they be detected with much sensitivity. Fig. 2b shows that TcO_4^- can be detected with reasonable sensitivity and that the aged carrier B contains no appreciable amount of pertechnetate. Fig. 2d shows that carrier A contains only the neutral and cationic products, whereas carrier B is much less completely aquated at the time it was used. Thus amounts of the two carriers giving equal technetium concentrations do not give equal concentrations of each of the aquation products. The concentrations of the neutral and, or, cationic products will be greater for carrier A solution. Electrophoretic examination showed that carrier A contained a high proportion of the neutral species while carrier B contained more of the cationic product.

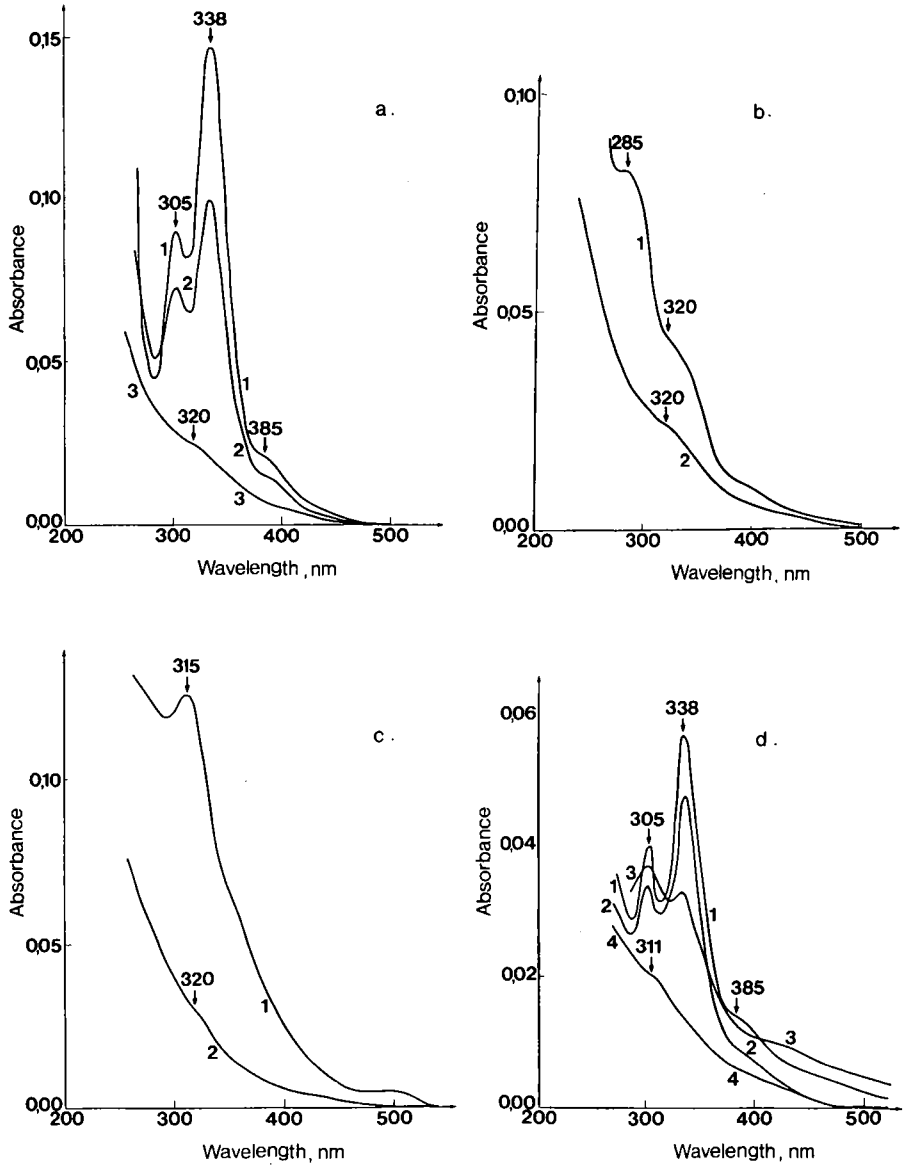

Fig. 2. Absorption spectra

a. $TcCl_6^{2-}$ (4.5×10^{-3} *M*) in CH_3COOH/CH_3COONa, pH = 2.8.
1 – 1 h, 2 – 96 h, 3 – 168 h.

b. Solution used in a. after 168 h.
1 – with a little TcO_4^-
2 – without added TcO_4^-

c. Spectra of electrophoretically separated neutral and cationic species from carrier B.
1 – neutral
2 – cationic

d. (i) Carrier B solution, technetium concentration, 5×10^{-4} *M*.
1 – 1 h, 2 – 20 h.
(ii) Carrier A solution, technetium concentration, 3.5×10^{-4} *M*.
3 – 1 h, 4 – 20 h.

3.3. Influence of the cation

Results of measurements under the same conditions, showed no difference between the solutions of the lithium and potassium salts at low concentrations of pertechnetate. But in the region where the proportion of $^{95g}TcO_4^-$ is rising with pertechnetate concentration the potassium salt gives a higher retention as $^{95g}TcO_4^-$. Addition of potassium sulphate to the solution of the lithium salt increases the retention to the value shown by a solution of the potassium salt. Addition of lithium sulphate to a solution of the potassium salt has not effect. The data are recorded in Table 5.

A similar increase was found, using carrier A at a concentration of 7.5×10^{-4} *M*. On addition of potassium sulphate to solution of lithium pertechnetate, 6×10^{-3} *M* in TcO_4^-, the proportion of $^{95g}TcO_4^-$ increases from 43.1% to 46.1%.

3.4. Effect of radical scavengers

It was found that addition of sodium or lithium perchlorate up to 3×10^{-3} *M* did not change the distribution of ^{95g}Tc in 6×10^{-3} *M* lithium pertechnetate solutions. Dissolved inert salts do not affect the distribution.

Table 5. *All experiments using Carrier B*

Conc. of Tc due to carrier (M)	Conc. of $^{99}TcO_4^-$ (M)	Added salt and conc. (M)	$^{95g}TcO_4^-$ (%)	
			$KTcO_4$	$LiTcO_4$
4.5×10^{-3}	carrier-free	–	27.5 ± 1.6	28.6 ± 2.6
4.0×10^{-4}	6×10^{-5}	–	27.5 ± 2.1	28.2 ± 1.5
4.0×10^{-4}	6×10^{-3}	–	38.8 ± 2.7	33.7 ± 2.8
4.0×10^{-4}	6×10^{-3}	K_2SO_4, 3×10^{-3}	–	38.7 ± 2.9
4.0×10^{-4}	6×10^{-3}	Li_2SO_4, 3×10^{-3}	38.6 ± 1.7	–

Table 6. *Influence of some radical scavengers on chemical distribution of* ^{95g}Tc *for* 6×10^{-3} *M* $Li^{99(95m)}TcO_4$ *solution* Carrier A (7.5×10^{-4} *M*)

System	Radical scavengers (M)	$^{95g}TcO_4^-$ (%)	Uncharged species (%)	Cationic species (%)	Anionic species (%)
1	–	43.1 ± 2.5	19.4 ± 1.3	24.2 ± 0.7	13.3 ± 2.1
2	C_2H_5OH (50%) pH 3	52.6 ± 2.8	14.9 ± 3.1	5.9 ± 0.9	26.6 ± 3.4
3	Phenol 10^{-4}	51.8 ± 3.7	11.0 ± 1.7	18.7 ± 1.8	18.5 ± 2.6
4	I_2 10^{-4}	57.7 ± 3.0	12.1 ± 1.6	14.5 ± 2.1	15.7 ± 4.1
5	$AgNO_3$ 10^{-4}	48.0 ± 4.7	14.9 ± 3.1	21.8 ± 3.6	15.3 ± 1.8
6	KNO_3 10^{-4}	57.4 ± 2.9	10.9 ± 1.9	13.3 ± 0.9	18.4 ± 3.4
	KNO_3 6×10^{-3}	60.9 ± 2.9	10.3 ± 1.9	11.9 ± 1.7	16.9 ± 1.9
7	$CuSO_4$ 10^{-4}	53.3 ± 2.4	14.0 ± 1.8	19.1 ± 2.4	13.6 ± 2.9
8	O_2	51.5 ± 2.9	14.1 ± 3.8	24.2 ± 1.9	10.2 ± 5.6

One might expect the ^{95g}Tc distribution to be affected by the radical products of the local radiolysis of the solvent by the Auger electrons. Experiments chosen to explore this possibility are reported in Table 6. Scavenging solutes 2 and 3 might be expected to remove hydroxyl radicals, 4, 5 and 6 react with solvated electrons and, or, hydrogen atoms, 8 should enhance HO_2 formation and 7 should remove HO_2. These experiments were performed with nitrogen saturated solutions, so that dissolved oxygen was not rigorously eliminated.

4. Discussion

(i) Concerning the carriers and their effects

The absorption spectra suggest that in the neutral and cationic aquation species the technetium has lost all its chloride ligands. Speculation regarding the chemical identity of these products has appeared elsewhere [2].

The difference in the behaviour of the two carriers used appears to be due to differences in the amounts of the neutral and cationic aquation products that they contain. These products can be separated electrophoretically and the technetium content of the regions of the paper strip containing the different species assayed. But this will not necessarily enable one to compare the behaviour of one carrier preparation with another since the proportion of neutral species in true solution may be more important than the total amount, which includes any colloidal material.

The more important result is that the proportion of $^{95g}TcO_4^-$ found is dependent on the amount of carrier present in the solution. Some pregenitor of part of the $^{95g}TcO_4^-$ found in a carrier free system can react with, or is protected by, modest concentrations of Tc(IV) species. The effect is noticeable at carrier concentrations (e.g. 4.4×10^{-4} *M*) too low for any hot reactions to be involved. The maximum change in retention as $^{95g}TcO_4^-$ produced implies that at least 40% of the isomeric transition product ^{95g}Tc species can interact with the carrier in this way.

(ii) The identity of the products

The products of isomeric transition, other than $^{95g}TcO_4^-$, appear to be the same as those found after isomeric transition in the solid pertechnetates, followed by solution in an aqueous medium [3]. Their easy oxidation to pertechnetate shows that they are derivatives of oxidation state less than seven. The electrophoretic behaviour of the neutral and cationic species is the same as those obtained by the aquation of $TcCl_6^{2-}$.

The anionic product, which is less affected by the composition of the aqueous medium, must also be a species of oxidation state less than seven.

(iii) The effect of the macroscopic pertechnetate concentration

At all concentrations of carriers the retention as $^{95g}TcO_4^-$ rises above a total concentration of pertechnetate of about 2×10^{-3} *M*. This implies a species containing ^{95g}Tc that can participate in an exchange reaction with TcO_4^-. Such a reaction could occur by oxygen transfer to a ligand deficient ^{95g}Tc species or by electron transfer with TcO_4^{n-} ($n = -1, 0, 2$). The latter possibility receives support from the observation that in the pertechnetate

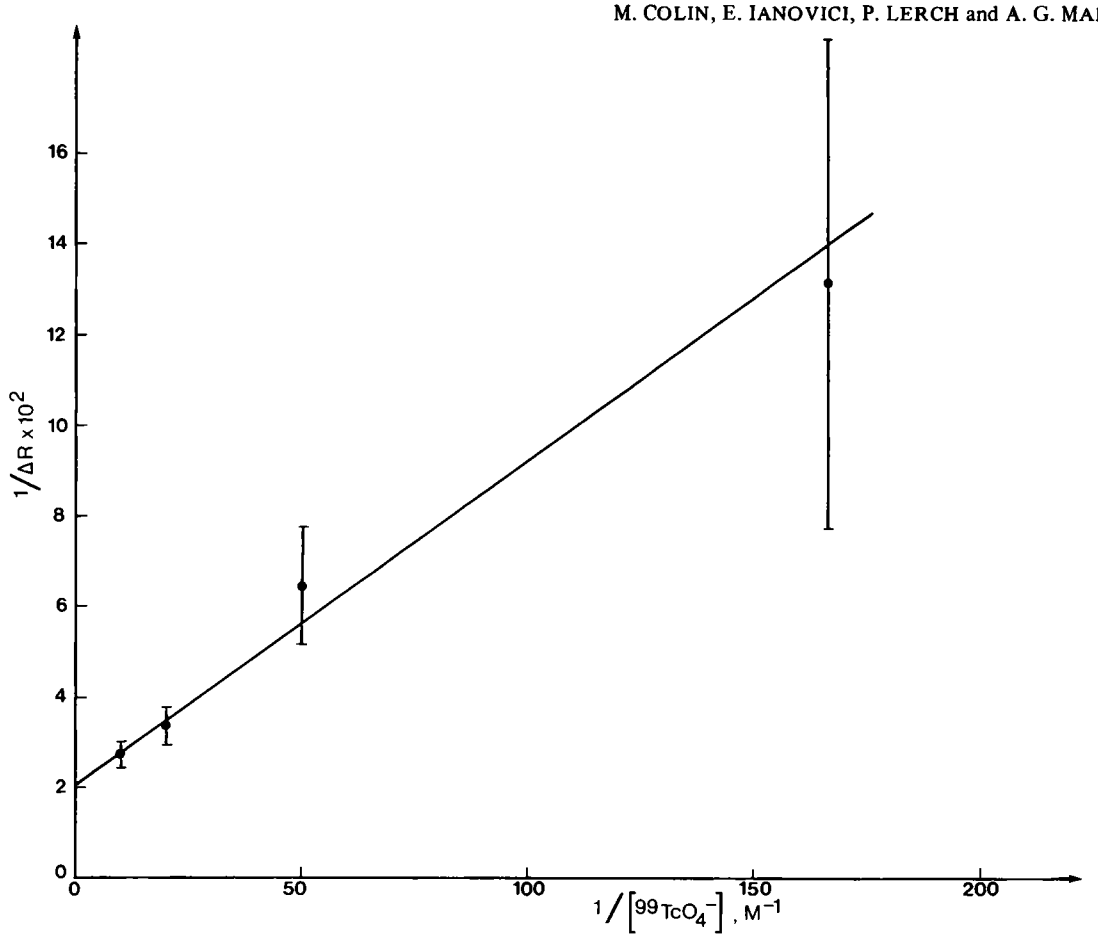

Fig. 3. Plot of $1/R - R_p$ versus $1/[TcO_4^-]$. (R_p: plateau retention as $^{95g}TcO_4^-$ at low $[TcO_4^-]$)

concentration region where this reaction is important, but not at lower concentrations, the increase in $^{95g}TcO_4^-$ is enhanced by replacing lithium ions by potassium. It is well known that electron transfer exchange between anions is susceptible to such catalysis [4], very likely because in the presence of the larger cations easier close approach of the interacting anions becomes possible.

This evidence suggests some part of the ^{95g}Tc forms a species that either exchange with TcO_4^- or suffer reduction by water, the two processes being in competition. This implies a linear relation between $1/[TcO_4^-]$ and $1/\Delta R$, where ΔR is the change in retention from the plateau value, R_p, at low $[TcO_4^-]$ (say at 10^{-4} M) to the value at the chosen $[TcO_4^-]$, all measurements being made at constant carrier concentration. Assuming that all the fraction $100 - R_p$ can participate in such competitive reactions we obtain Fig. 3.

Other interpretations are possible, but the above requires the least assumptions.

(iv) Effects due to Auger autoradiolysis

Surrounding the molecule affected by the isomeric transition will be a small region in which some positive charge may be acquired by electron transfer limiting the charge build up on the affected atom and molecule. The technetium containing fragment is unlikely to acquire great kinetic energy by any coulombic bond rupture. A rather larger volume around the site of the transition will contain radiolytic products arising from the Auger electrons. In the case of ^{95g}Tc, the majority of the Auger electrons will have kinetic energies less than 2 keV and the greater part of their radiolytic effect will occur within a sphere of radius about 300 Å around the ^{95g}Tc atom. Since the pertechnetate concentration effect indicates diffusive reactions of the ^{95g}Tc species are important one might expect effects due to products of autoradiolysis of the water.

Scavenger solutes were chosen that should remove $OH^\bullet$ (N°2 and N°3), electrons (N°4, N°5 and N°6) and reduce (N°7) or enhance (N°8) $HO_2^\bullet$. The results are somewhat unexpected. All the solutes gave some increase, beyond any experimental error, in $^{95g}TcO_4^-$, even the two that should eliminate $OH^\bullet$. Two of the electron scavengers (N°4 and N°6) led to rather large increases in $^{95g}TcO_4^-$, as might be expected, but conversion to $HO_2^\bullet$ by oxygen saturation only gave a more modest increase. However solutes expected to be inert proved to be so. More detailed studies of these effects will be necessary.

References

1. IANOVICI, E., LERCH, P., ZAHNER, G., MADDOCK, A. G.: Radiochim. Acta **29**, 79 (1981).
2a. KOYAMA, M., KANCHIKU, Y., FUJINAGA, T.: Coord. Chem. Rev. **3**, 285 (1968).
b. KANCHIKU, Y.: Bull. Chem. Soc. Japan **42**, 2831 (1969).
c. IANOVICI, E., KOSINSKI, M., LERCH, P., MADDOCK, A. G.: J. Radioanal. Chem. Soc. **64**, 315 (1981).
3. IANOVICI, E., LERCH, P., PROSO, Z., ZAHNER, G., MADDOCK, A. G.: Radiochim. Acta **28**, 57 (1981).
4a. SHEPPARD, J. C., WAHL, A. C.: J. Am. Chem. Soc. **79**, 1020 (1957).
b. GJERTSEN, A. G., WAHL, A. C.: J. Am. Chem. Soc. **81**, 1572 (1959).